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(54) [Title of the Invention] ELECTROPHOTOGRAPHIC PHOTORECEPTOR, ELECTROPHOTOGRAPHIC METHOD,

ELECTROPHOTOGRAPHIC APPARATUS, AND PROCESS CARTRIDGE FOR ELECTROPHOTOGRAPHIC APPARATUS

(57) [Abstract]

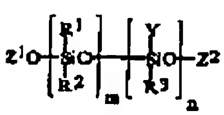
[Object]

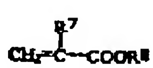
To provide an electrophotographic photoreceptor having high sensitivity and high durability, and an electrophotographic apparatus and a process cartridge, using the photoreceptor.

[Solution Means]

In an electrophotographic photoreceptor having at least a photosensitive layer and a protective layer formed sequentially on a conductive support, the protective layer contains an inorganic filler and an acryl modified polyorganosiloxane compound having an acrylic polymer grafted to a silicone main chain. As the acryl modified polyorganosiloxane compound, an acryl modified polyorganosiloxane prepared by emulsion graft copolymerization of a mixture of polyorganosiloxane represented by a general formula (I), and (meth)acrylate represented by a general formula (II) or a monomer capable of copolymerizing with the (meth)acrylate can be used.

[Chemical Formula 1]


......(I)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[Scope of Claims for Patent]

[Claim 1]

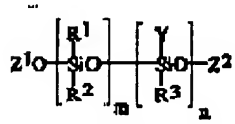
An electrophotographic photoreceptor comprising a conductive support and at least a photosensitive layer and a protective layer formed sequentially on the conductive support, wherein the protective layer contains an inorganic filler and an acryl modified polyorganosiloxane compound having an acrylic polymer grafted to a silicone main chain.

[Claim 2]

The electrophotographic photoreceptor according to claim 1, wherein the acryl modified polyorganosiloxane compound is an acryl modified polyorganosiloxane obtained by emulsion graft copolymerization of polyorganosiloxane represented by a general formula (I):

[Chemical Formula 1]

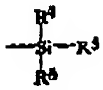
General formula (I)



.......(I)

wherein, R^1, R^2 and R^3 are the same or different and each represents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated hydrocarbon group; Y represents an organic group having a radical reactive group and/or a SH group; Z^1 and Z^2 are the same or different and each represents a hydrogen atom, a lower alkyl group, or a group represented by the following formula:

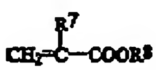
[Chemical Formula 2]



wherein, R^4 and R^5 are the same or different and each represents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated hydrocarbon group, R^6 represents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated hydrocarbon group, or an organic group having a radical reactive group and/or a SH group; m represents a positive integer of 10,000 or less; and n represents an integer of 1 or more with (meth)acrylate represented by a general formula (II):

[Chemical Formula 3]

General formula (II)



----(II)

wherein R^7 represents a hydrogen atom or a methyl group; and R^8 represents an alkyl group, an alkoxy-substituted alkyl group, a cycloalkyl group, or an aryl group) or a mixture of 70% by weight or more of the (meth)acrylate and 30% by weight or less of a copolymerizable monomer, in a mixing ratio (by weight) of 5:95 to 95:5.

[Claim 3]

The electrophotographic photoreceptor according to claim 2, wherein the weight of the polyorganosiloxane represented by the general formula (I) is more than the weight of the (meth)acrylate represented by the general formula (II) or the mixture of 70% by weight or more of the (meth)acrylate and 30%

by weight or less of the copolymerizable monomer.

[Claim 4]

The electrophotographic photoreceptor according to any one of claims 1 to 3, wherein the acryl modified polyorganosiloxane compound is granularly dispersed in the protective layer.

[Claim 5]

The electrophotographic photoreceptor according to any one of claims 1 to 4, wherein the acryl modified polyorganosiloxane compound is in the form of a micro gel.

[Claim 6]

The electrophotographic photoreceptor according to any one of claims 1 to 5, wherein the inorganic filler contained in the protective layer is at least one kind of metal oxide.

[Claim 7]

The electrophotographic photoreceptor according to claim 6, wherein at least one kind of the metal oxide contained in the protective layer is subjected to surface treatment using at least one kind of a surface treating agent.

[Claim 8]

The electrophotographic photoreceptor according to any one of claims 1 to 7, wherein the protective layer contains at least one kind of a charge transport material.

[Claim 9]

The electrophotographic photoreceptor according to any

one of claims 1 to 9, wherein the protective layer contains at least any one of a polycarbonate resin and a polyallylate resin, or a mixture of them.

[Claim 10]

An electrophotographic method comprising the step of repeatedly carrying out at least charging, image exposing, developing, transferring, cleaning, and diselectrifying of an electrophotographic photoreceptor, wherein the electrophotographic photoreceptor is the electrophotographic photoreceptor according to any one of claims 1 to 9.

[Claim 11]

An electrophotographic apparatus comprising at least charging means, image exposing means, developing means, transfer means, and an electrophotographic photoreceptor, wherein the electrophotographic photoreceptor is the electrophotographic photoreceptor according to any one of claims 1 to 9.

[Claim 12]

A process cartridge for an electrophotographic apparatus comprising at least an electrophotographic photoreceptor, wherein the electrophotographic photoreceptor is the electrophotographic photoreceptor according to any one of claims 1 to 9.

[Claim 13]

An electrophotographic apparatus comprising the process cartridge according to claim 12 installed therein.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an electrophotographic photoreceptor having high durability and capable of outputting a stable image without causing deterioration of image quality even when repeatedly used for a long period. Further, the present invention relates to an electrophotographic method, an electrophotographic apparatus, and a process cartridge for an electrophotography, which use these electrophotographic photoreceptors.

[0002]

[Prior Art]

In recent years, an electrophotographic type information processing system has been remarkably improved. Particularly, a laser printer and a digital copying machine, which record information with light by converting the information into a digital signal, are remarkably improved in the print quality and reliability. Further, these devices are applied to a laser printer or a digital copying machine, which can carry out full color printing, by harmonizing with a high speed technology. Thus, as for a required function of a photoreceptor, it is particularly important to compatibly have high image quality and high durability.

[0003]

As for a photoreceptor used for the electrophotographic typed laser printer or digital copying machine, a photoreceptor using an organic photosensitive material has been widely used from the viewpoints of a low cost, productivity, non-pollution property, and the like. As an organic electrophotographic photoreceptor, a photoreceptor of a photoconductive resin represented by polyvinyl carbazole (PVK), a charge transfer complex type photoreceptor represented by PVK-TNF (2,4,7-trinitrofluorenone), a pigment dispersant type photoreceptor represented by a phthalocyanine-binder, a functionally separated type photoreceptor in which a charge generating material and a charge transport material are used in combination, and the like have been known.

[0004]

In a mechanism to from an electrostatic latent image in the functionally separated photoreceptor, when a photoreceptor is charged and then irradiated with light, light passes through a charge transport layer and absorbed by a charge generating material in a charge generating layer to generate charge. The generated charge is injected into the charge transport layer at the interface between the charge generating layer and the charge transport layer and transferred in the charge transport layer by an electric field. The transferred charge neutralizes a surface charge to form an electrostatic latent image.

[0005]

However, when the organic photoreceptor is repeatedly used, film scraping is likely to occur. As the film scraping of a photosensitive layer becomes severe, decrease of an electrification potential and deterioration of optical sensitivity of the photoreceptor, background stains due to surface crack of the photoreceptor and deterioration of image quality such as decrease in an image density tend to be promoted. Thus, abrasion resistance has hitherto been considered as a large problem of the photoreceptor. Further, in accordance with speeding-up of the electrophotographic apparatus or reduction in a diameter of the photoreceptor due to size reduction of the apparatus, it has recently become more important to make a photoreceptor to have higher durability.

[0006]

As a method for realizing a photoreceptor having high durability, there are widely known a method in which a protective layer is formed on an outermost surface of a photoreceptor to impart lubricity to the oprotective layer, a method of curing a protective layer, and a method of containing a filler in a protective layer. Particularly, the method of containing a filler in a protective layer is remarkably effective to make a photoreceptor to have high durability. Mechanical durability of the photoreceptor, such as improvement in abrasion resistance, is improved by containing a filler in a protective layer. However, in addition to the mechanical durability, electric durability

such as stability of electrification potential and potential of the exposed area is also remarkably important due to repeatedly charging and exposing in an electrophotographic type imaging. The reason is that, even if the mechanical durability is improved and the amount of film scraping remarkably decreases, it becomes impossible to obtain sufficient electrostatic contrast when the electrification potential decreases or the potential of the exposed area increases. As a result, an image deteriorates.

[0007]

On the other hand, the cleaning property of a photoreceptor is also an important characteristic to maintain high image quality. When foreign substances are adhered on the surface of a photoreceptor, various image defects occur, and thus an image cannot be outputted for a long period. Particularly, since a photoreceptor containing a filler in the protective layer and having low mechanical abrasion is not scraped, the cleaning property is more important. Further, the particle size of a toner used for electrophotography tends to become small in order to response to a request to output a high quality image having like a photographic tone. When the toner diameter decreases, the cleaning property of a photoreceptor may deteriorate. Furthermore, a spherical toner by a polymerization is considered relating to the small diameter toner. However, the spherical toner has less cleaning property than that of a conventional pulverized toner. Therefore, in order to make a photoreceptor

to have high durability and high image quality, it is necessary to improve the cleaning property of the photoreceptor.

[0008]

As a method for improving the cleaning property, it is effective to reduce a friction coefficient on the surface of a photoreceptor. By reducing the friction coefficient, abrasion resistance becomes sufficient, and the cleaning property and abrasion resistance can be expected to be compatible. Japanese Unexamined Patent Publication Nos. 07-295248, 07-301936, 08-082940, and the like propose that a fluorine modified silicone oil is contained in the surface layer, thereby improving the surface property, improving the cleaning property, and improving the abrasion resistance of the surface of the photoreceptor. However, when fluorine modified silicone oil is contained in the surface layer, the fluorine modified silicone oil transfers closing to the surface during a process of forming the surface layer, and is concentrated on the portion neighboring the surface. Thus, the effect is lost in an early stage due to abrasion of the surface layer by repeatedly using a photoreceptor.

[0009]

Further, various trials have been made on a system in which fine particles are added in order to improve abrasion resistance. For example, the addition of silicone resin fine particles, the addition of fluorine-containing resin fine particles (Japanese

Unexamined Patent Publication No. 63-65449) and the addition of melamine resin fine particles (Japanese Unexamined Patent Publication No. 60-177349) are proposed. Japanese Unexamined Patent Publication No. 02-143257 proposes a method in which a polyethylene powder is contained in a surface layer, thereby reducing a friction coefficient of the surface layer, improving cleaning property, and improving abrasion resistance of the photoreceptor. Further, Japanese Unexamined Patent Publication No. 02-144550 proposes a method in which a fluorine resin-containing powder is contained in a surface layer, thereby reducing a friction coefficient of the surface layer, improving cleaning property, and improving abrasion resistance of the photoreceptor. Further, Japanese Unexamined Patent Publication Nos. 07-128872 and 10-254160 propose a method in which silicone fine particles are contained in a surface layer, thereby reducing a friction coefficient of the surface layer, improving cleaning property, and improving abrasion resistance of the photoreceptor. Further, Japanese Unexamined Patent Publication No. 2000-010322 and U.S. Patent No. 5,998,072 propose a method in which crosslinking type organic fine particles are contained in a surface layer, thereby reducing a friction coefficient of the surface layer, improving cleaning property, and improving abrasion resistance of the photoreceptor. Furthermore, Japanese Unexamined Patent Publication No. 08-190213 proposes a method in which methylsiloxane resin fine

particles are contained in a surface layer, thereby reducing a friction coefficient of the surface layer, improving cleaning property, and improving abrasion resistance of the photoreceptor. These methods are proposed so as to achieve high durability by imparting functions such as reduction in a friction coefficient of the surface of a photoreceptor and reduction in surface energy. However, these methods have the following problems.

[0010]

That is, when a resin powder or fine particles are dispersed in a surface layer, thereby improving durability of the surface of a photoreceptor, since compatibility with a binder resin is poor, the resin powder or fine particle s are not sufficiently dispersed. As a result, abnormal defects such as black spots and white spots occur upon formation of an image, and thus there is a problem that residual potential increases during repeatedly using the photoreceptor. Further, since light transmission properties of a photosensitive layer are prevented, sensitivity decreases and charge transport property decreases. Thus, there is a problem that an image density is uneven. These problems have never been solved.

[0011]

Further, when polytetrafluoroethylene fine particles or organopolysiloxane fine particles are added, the effect to reduce a friction coefficient is low, and abrasion resistance is not sufficiently improved. Further, even when mechanical

durability such as abrasion resistance is improved, a photoreceptor is exposed by an active gas such as ozone generated upon discharging during charging, and an active gas existing in a circumference environment, e.g., nitrogen oxide gas generated from a heating appliance, and the like, during repeatedly using for a long period. Thus, the surface of a photoreceptor is influenced by these gases, thereby deteriorating an image in many cases. By the exposure, there is in the tendency that a friction coefficient of the surface of a photoreceptor increases, and thus a low friction coefficient cannot be maintained.

[0012]

In this phenomenon, in particular, when abrasion resistance increases largely, that is, when the amount of film scraping is largely reduced in a photoreceptor, like a conventional photoreceptor having a large amount of film scraping, the photoreceptor cannot be expected to have an effect in which a new outer most surface is automatically refaced by sequentially abrading from the surface to gradually abrade and polish the outer most surface. The outer most surface is polluted by an active gas, an adhered corona generated product, and a reaction of the active gas or a corona discharge. Therefore, there is a problem that an image is deteriorated as a result of surface pollution, that is, an abnormal image is likely to occur.

[0013]

As described above, the photoreceptor having high abrasion resistance has problems that image deterioration and generation of an abnormal image due to poor cleaning, modification of the surface of the photoreceptor by an active gas occur as compared with a photoreceptor having no high abrasion resistance. That is, has never been obtained a high durability electrophotographic photoreceptor, which can improve mechanical durability and has excellent cleaning property, and is also less likely to cause adhesion of foreign substances and has excellent electrical durability and chemical durability, and can stably form a high quality image even when repeatedly used for a long period.

[0014]

[Problems to be solved by the Invention]

An object of the present invention is to provide a high durability photoreceptor, which scarcely causes abrasion and is excellent in cleaning property from an initial stage for a long period, and also causes neither an increase in residual potential or an abnormal image such as image blur for a long period of time and can stably form a high quality image for a long period. Further, another object of the present invention is to provide an electrophotographic method, an electrophotographic apparatus, and a process cartridge for electrophotography, which do not require replacement of a photoreceptor and realize high-speed printing or size reduction of the apparatus due to reduction in diameter of the photoreceptor,

and also can stably form a high quality image for a long period of time, by using the photoreceptor.

[0015]

[Means for Solving the Problems]

The present inventors have intensively studied and found that an electrophotographic photoreceptor including a filler dispersing type protective layer having excellent abrasion resistance, which is excellent in cleaning property and causes neither filming nor generation of an abnormal image due to poor cleaning even when repeatedly used for a long period, and also suppress generation of an abnormal image caused by a decrease in an electrification potential or increase in a residual potential, by containing an inorganic filler and a specific silicone compound in the protective layer.

[0016]

With the configurations described in the following (1) to (13), it becomes possible to provide an electrophotographic photoreceptor which can achieve both high durability and high image quality and stably form a high quality image even when repeatedly used for a long period, and to provide an electrophotographic method, an electrophotographic apparatus, and a process cartridge for electrophotography, which can stably form a high quality image even when repeatedly used.

[0017]

(1) An electrophotographic photoreceptor including a

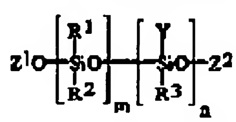
conductive support and at least a photosensitive layer and a protective layer formed sequentially on the conductive support, wherein the protective layer contains an inorganic filler and an acryl modified polyorganosiloxane compound having an acrylic polymer grafted to a silicone main chain.

[0018]

(2) The electrophotographic photoreceptor according to (1), wherein the acryl modified polyorganosiloxane compound is an acryl modified polyorganosiloxane obtained by emulsion graft copolymerization of polyorganosiloxane represented by a general formula (I):

[Chemical Formula 4]

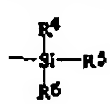
General formula (I)



......(I)

wherein, R^1, R^2 and R^3 are the same or different and each represents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated hydrocarbon group; Y represents an organic group having a radical reactive group and/or a SH group; Z^1 and Z^2 are the same or different and each represents a hydrogen atom, a lower alkyl group, or a group represented by the following formula:

[Chemical Formula 5]



wherein, R^4 and R^5 are the same or different and each represents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated

hydrocarbon group, R^6 represents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated hydrocarbon group, or an organic group having a radical reactive group and/or a SH group); m represents a positive integer of 10,000 or less; and n represents an integer of 1 or more with (meth)acrylate represented by a general formula (II):

[Chemical Formula 6]

General formula (II)

$$CH_2{=}\overset{R^7}{\overset{|}{C}}{-}COOR^8 \quad \cdots\cdots(II)$$

wherein R^7 represents a hydrogen atom or a methyl group; and R^8 represents an alkyl group, an alkoxy-substituted alkyl group, a cycloalkyl group, or an aryl group) or a mixture of 70% by weight or more of the (meth)acrylate and 30% by weight or less of a copolymerizable monomer in a mixing ratio (by weight) of 5:95 to 95:5.

[0019]

(3) The electrophotographic photoreceptor according to (2), wherein the weight of the polyorganosiloxane represented by the general formula (I) is more than the weight of the (meth)acrylate represented by the general formula (II) or the mixture of 70% by weight or more of the (meth)acrylate and 30% by weight or less of the copolymerizable monomer.

[0020]

(4) The electrophotographic photoreceptor according to any one of (1) to (3), wherein the acryl modified

polyorganosiloxane compound is granularly dispersed in the protective layer.

[0021]

(5) The electrophotographic photoreceptor according to any one of (1) to (4), wherein the acryl modified polyorganosiloxane compound is in the form of a micro gel.

[0022]

(6) The electrophotographic photoreceptor according to any one of (1) to (5), wherein the inorganic filler contained in the protective layer is at least one kind of metal oxide.

[0023]

(7) The electrophotographic photoreceptor according to (6), wherein at least one kind of the metal oxide contained in the protective layer is subjected to surface treatment using at least one kind of a surface treating agent.

[0024]

(8) The electrophotographic photoreceptor according to any one of (1) to (7), wherein the protective layer contains at least one kind of a charge transport material.

[0025]

(9) The electrophotographic photoreceptor according to any one of (1) to (9), wherein the protective layer contains at least any one of a polycarbonate resin and a polyallylate resin, or a mixture of them.

[0026]

(10) An electrophotographic method including the step of repeatedly carrying out at least charging, image exposing, developing, transferring, cleaning, and diselectrifying of an electrophotographic photoreceptor, wherein the electrophotographic photoreceptor is the electrophotographic photoreceptor according to any one of (1) to (9).

[0027]

(11) An electrophotographic apparatus including at least charging means, image exposing means, developing means, transfer means, and an electrophotographic photoreceptor, wherein the electrophotographic photoreceptor is the electrophotographic photoreceptor according to any one of (1) to (9).

[0028]

(12) A process cartridge for an electrophotographic apparatus including at least an electrophotographic photoreceptor, wherein the electrophotographic photoreceptor is the electrophotographic photoreceptor according to any one of (1) to (9).

[0029]

(13) An electrophotographic apparatus including the process cartridge according to (12) installed therein.

[0030]

The above respective inventions will now be described.

<u>Relating to (1)</u>

As described in the prior art, when only an inorganic filler is contained, abrasion resistance is largely improved but lubricity of a photoreceptor decreases. Thus, noise or reversing of a blade easily generates, or foreign substances are easily adhered on a photoreceptor, and thus poor filing or an abnormal image due to insufficient cleaning is likely to occur. On the other hand, when only an acryl modified polyorganosiloxane compound is contained, there are problems that the content of a siloxane structural part is necessarily restricted in order to consider mechanical strength and abrasion resistance cannot be largely improved. In the present invention, functions are separated, that is, abrasion resistance is mainly improved by adding the inorganic filler, and decrease of surface energy and improvement of lubricity are mainly obtained by adding the acryl modified polyorganosiloxane compound. Thus, designing and treating to more exert each function to the maximum than a system, which is added by respectively and independently, can be obtained. The present invention can make a photoreceptor to have abrasion resistance, lubricity, and a foreign substance removing property in the well balance for the first time. In addition, expanding potential variation during repeatedly using, which is a fault of an inorganic filler-added system, can be suppressed, so that an organic photoreceptor having stable electric property can be provided. The acryl modified polyorganosiloxane compound used in the present invention exhibits foreign substance removing

property at the siloxane structural part by the lubricity and low surface energizing. The effect to exhibit this property is higher when a dimethyl silicone chain is longer. Further, in the case of a general silicone oil and a silicone resin, since these oil and resin are not uniformly dispersed in a film or segregated on the surface, it is considered that these oil and resin are easily removed at the time of operating processing and supplying these materials from the inside of a film is not carried out. As a result of this, lubricity and foreign substance removing property cannot be maintained. The acryl modified polyorganosiloxane compound has acryl polymer parts. However, in order to increase compatibility with a medium, an acryl polymer parts are necessarily taken-in somewhat uniformly. In order to take-in it in this way, it is advantage to take a chemical structure in which acryl polymers are grafted at some parts of a silicone main chain having a comparatively long molecule chain. Since the acryl modified polyorganosiloxane compound has increased compatibility with a protective layer structuring material, bonding property of the acryl modified polyorganosiloxane compound to the medium of the protective layer increases so that the compound is not easily removed. Thus, the acryl modified polyorganosiloxane compound can exert its effect for a long period. Further, the inorganic filler-added system has faults that residual potential due to charge trap easily generates and light area potential during repeatedly using

increases. When a resin and fine particles are added to such a system as an additive, potential may increase more. Thus, there is a problem that a photoreceptor has low potential contrast to easily generate an abnormal image. However, in the case of the acryl modified polyorganosiloxane used in the present invention, there is no synergy effect due to mixing, and increasing potential can be suppressed as much as possible even when enough amounts of the acryl modified polyorganosiloxane are added in the system. Thus, an organic photoreceptor having stable electrical property can be provided. As described above, since the present invention includes the inorganic filler and the acryl modified polyorganosiloxane compound, the photoreceptor can have a compatibility of lubricity and low surface energy with a medium while maintaining an excellent potential property.

[0031]

Relating to (2)

The acryl modified polyorganosiloxane compound having a structure indicated in the above (2) can sufficiently exhibits lubricity, foreign substance removing property, and compatibility with a medium, which are described in the above (1). Further, the acryl modified polyorganosiloxane compound has few side effects to electrophotographic property of a photoreceptor. Thus, enough amounts of the compound can be contained in a film. This is one of large characteristics of

the present invention, and has an effect to improve durability.

[0032]

Relating to (3)

With the composition ratio indicated in the above (3), a photoreceptor having more excellent lubricity and foreign substance removing property can be provided.

[0033]

Relating to (4)

The acryl modified polyorganosiloxane compound is to exhibits lubricity and low surface energy at an organosiloxane part, and exhibits compatibility at an acryl polymerization part, as described above. However, in order to increase lubricity of a photoreceptor, a film in which the siloxane part is partially, unevenly dispersed having a high density is more advantageous than a film in which the siloxane part is uniformly dispersed having a low density when these films are compared at the same density. As for such a method, an acryl modified polyorganosiloxane compound is granularly dispersed. By forming such a dispersing film, excellent lubricity and foreign substance removing property can be realized in a system in which comparatively few amounts of the compound are added.

[0034]

Relating to (5)

A photoreceptor is produced by dispersing or dissolving an additive in a preferable solvent such as a binder. At this

time, in order to form a granular film having good dispersibility, it is preferable that an acryl modified polyorganosiloxane compound is partially insolubilized to maintain the form of particle in a coating solution. A proper example of this is in the form of a micro gel. When an acryl modified polyorganosiloxane compound in the form of a micro gel is used, a protective layer in which the compound is uniformly dispersed in a fixed particle state can be easily formed. A photoreceptor capable of having lubricity and foreign substance removing property, and maintaining these properties can be provided.

[0035]

Relating to (6)

Higher electric resistance of a protective layer is proper, and background stains of an image or decreasing of resolution is caused under low electric resistance. A metal oxide has high insulation and high hardness, and thus the metal oxide is proper as the inorganic filler for a protective layer. By using the metal oxide, a photoreceptor which has abrasion resistance, electrostatic stability, a good combination with an acryl modified polyorganosiloxane compound, few abrasion scrapping, and high image stability can be provided.

[0036]

Relating to (7)

Most of the surface of a filler has high polarity, and a photoreceptor generally using a binder having low polarity

has a problem in dispersibility. When a metal oxide inorganic filler subjected to a surface treatment is used, dispersibility of the filler increases, and a protective layer also having excellent dispersibility of an acryl modified polyorganosiloxane compound can be formed.

[0037]

Relating to (8)

A protective layer in which the inorganic filler and the acryl modified polyorganosiloxane compound are dispersed has properly the film thickness of several microns. However, even when the film thickness is several microns, a charge transport performance is low, and increasing residual potential or decreasing sensitivity is caused as for electrophotographic properties. In order to satisfy electrophotographic properties such as electrostatic property, the residual potential and sensitivity, addition of a charge transport material is effective. By adding the charge transport material, a photoreceptor having electrophotographic properties, which are similar to those of a photoreceptor not having a protective layer, and having excellent abrasion resistance, lubricity, and foreign substance removing property can be provided.

[0038]

Relating to (9)

A photoreceptor of the present invention can have abrasion resistance by adding the inorganic filler and maintain lubricity

and foreign substance removing property by adding the acryl modified polyorganosiloxane compound. However, properties given to the photoreceptor are difference depending on a binder resin as a main material of a protective layer medium. Abrasion resistance is largely improved by adding the inorganic filler to the binder resin having excellent abrasion resistance. Formation of a proper dispersing film and maintaining property are influenced by adding the inorganic filler to the resin which has excellent compatibility with the acryl modified polyorganosiloxane compound. Therefore, a binder having compatibility and mechanical strength in the well-balanced state is effective. As a result of consideration, when a polycarbonate resin or a polyallylate resin is used, a photoreceptor having excellent property to maintain excellent abrasion resistance, lubricity, and foreign substance removing property can be provided.

[0039]

<u>Relating to (10) to (13)</u>

As for an electrophotographic method, an electrophotographic apparatus and a process cartridge according to an electrophotographic process mounted with a photoreceptor described in the above (1) to (9), the exchange frequency of a photoreceptor is fewer than conventional ones because of increasing a life of a photoreceptor. Therefore, the number of maintenance is few and running cost is low. Furthermore,

a stable image can be outputted for a long period.

[0040]

[Embodiments of the Invention]

An electrophotographic photoreceptor used in the present invention will now be described with reference to the accompanying drawings.

[0041]

(Layer Structure of Photoreceptor)

FIG. 1 is a view showing a photoreceptor containing a photosensitive layer having a single layer structure. The photoreceptor includes a photosensitive layer 33 arranged on a conductive support 31, and a protective layer 39 arranged on the surface of the photosensitive layer 33. The conductive layer 33 mainly contains a charge generating material and a charge transport material. In this case, the protective layer 39 contains the acryl modified polyorganosiloxane compound and the inorganic filler. FIG. 2 is a view showing a photoreceptor containing a photosensitive layer having a laminated structure. The photoreceptor includes a photosensitive layer in which a charge generating layer 35 mainly containing a charge generating material and a charge transport layer 37 mainly containing a charge transport material are laminated on the conductive support 31, and a protective layer 39 on the charge transport layer. In this case, the protective layer 39 contains the acryl modified polyorganosiloxane compound and the inorganic filler. FIG. 3

shows another example of a photoreceptor containing a photosensitive layer having a laminated structure. The photoreceptor includes the photosensitive layer in which the charge transport layer 37 mainly containing a charge transport material and the charge generating layer 35 mainly containing a charge generating material are laminated on the conductive support 31, and the protective layer 39 on the charge generating layer. In this case, the protective layer 39 contains the acryl modified polyorganosiloxane compound and the inorganic filler.

[0042]

(Conductive Support)

The conductive support 31 is a formed conductive support having volume electric resistance of 10^{10} Ω•cm or less. For example, the support is a coated film-like or cylindrical plastic or a coated paper by vapor-depositing or sputtering a metal, such as aluminum, nickel, chromium, Nichrome, copper, gold, silver, and platinum, or metal oxide, such as tin oxide or indium oxide. Further, the support is a plate made of aluminum, an aluminum alloy, nickel, stainless steel, and the like or a surface treated pipe made by steps of making a rough pipe by extruding or drawing these metal plates and subjecting to a surface treatment of cutting, super-finishing or polishing. An endless nickel belt and an endless stainless steel belt, which are disclosed in Japanese Unexamined Patent Publication No. 52-36016, can be used as the conductive support 31.

[0043]

In addition, the conductive support 31 of the present invention can be made by dispersing a conductive powder in a proper binder resin and applying the dispersant obtained to the above support. Examples of the conductive powder include carbon black, acetylene black, a powder of a metal such as aluminum, nickel, iron, Nichrome, copper, zinc, and silver, or a fine powder of metal oxide such as conductive tin oxide or ITO.

[0044]

Examples of the binder resin used with the conductive powder include a thermoplastic resin, a thermosetting resin or photocurable resin, such as polystyrene, a styrene-acrylonitrile copolymer, a styrene-butadiene copolymer, a styrene-maleic anhydride copolymer, polyester, polyvinyl chloride, a vinyl chloride-vinyl acetate copolymer, polyvinyl acetate, polyvinylidene chloride, a polyallylate resin, a phenoxy resin, polycarbonate, a cellulose acetate resin, an ethyl cellulose resin, polyvinyl butyral, polyvinyl formal, polyvinyl toluene, poly-N-vinylcarbazole, an acryl resin, a silicone resin, an epoxy resin, a melamine resin, a urethane resin, a phenol resin or an alkyd resin. The conductive layer can be formed by dispersing these conductive powders and a binder resin in a proper solvent, such as tetrahydrofuran, dichloromethane, methyl ethyl ketone, or toluene, and applying the dispersant obtained.

[0045]

Further, as the conductive support 31 of the present invention, a conductive layer on a proper cylindrical substrate, where the conductive layer is formed by a heat shrinkable tube made by containing the above conductive powders in a material, such as polyvinyl chloride, polypropylene, polyester, polystyrene, polyvinylidene chloride, polyethylene, chlorinated rubber, and Teflon(registered trademark) can be preferably used.

[0046]

(Photosensitive layer)

A photosensitive layer will be described. A photosensitive layer of a photoreceptor used in the present invention may have a single layer structure or a laminated structure. However, in order to clearly describe, a case of the laminated structure containing the charge generating layer 35 and the charge transport layer 37 will be described at first.

[0047]

Charge Generating Layer

The charge generating layer 35 mainly contains a charge generating material. The charge generating layer 35 can use a publicly known charge generating material, and a typical example of the material includes a monoazo pigment, a disazo pigment, a trisazo pigment, a perylene-based pigment, a perynone-based pigment, a quinacridone-base pigment, a

quinone-based condensation polycyclic compound, a squalic acid-based pigment, another phthalocyanine-based pigment, a naphthalocyanine-based pigment, or an azlenium salt-based pigment, and these charge generating materials can used. These charge generating materials can be used independently or by mixing two or more kinds.

[0048]

The charge generating layer 35 can be formed by dispersing the charge generating material in a proper solvent with a binder resin if necessary using a ball mill, an attriter, a sand mill or a supersonic wave, and applying the dispersion to a conductive support, followed by drying.

[0049]

Examples of the binder resin used for the charge generating layer 35 if necessary include polyamide, polyurethane, an epoxy resin, polyketone, polycarbonate, a silicone resin, an acryl resin, polyvinyl butyral, polyvinyl formal, polyvinyl ketone, polystyrene, polysulfone, poly-N-vinylcarbazole, polyacrylamide, polyvinylbenzal, polyester, a phenoxy resin, a vinyl chloride-vinyl acetate copolymer, polyvinyl acetate, polyphenylene oxide, polyamide, polyvinyl pyridine, a cellulose-based resin, casein, polyvinyl alcohol, or polyvinyl pyrrolidone. The amount of the binder resin is 0 to 500 parts by weight with respect to 100 parts by weight of a charge generating material, and preferably 10 to 300 parts by weight. The binder

resin may be added before or after dispersing.

[0050]

Examples of the solvent used in the present invention include isopropanol, acetone, methyl ethyl ketone, cyclohexanone, tetrahydrofuran, dioxane, ethyl cellosolve, ethyl acetate, methyl acetate, dichloromethane, dichloroethane, monochlorobenzene, cyclohexane, toluene, xylene, or ligroin. Particularly, a ketone-based solvent, an ester-based solvent, or an ether-based solvent can be preferably used. These solvents may be used alone or in combination.

[0051]

The conductive layer 35 mainly contains a charge generating material, a solvent, and a binder resin. Further, the conductive layer 35 may contains a sensitizer, a dispersant, a surfactant agent, silicone oil, and the like. As a coating method of a coating solution, a dip coating method, a spray coat, a bead coat, a nozzle coat, a spinner coat, a ring coat, or the like can be used. The film thickness of the charge conductive layer 35 is suitably about 0.01 to 5 μm, and preferably 0.1 to 2 μm.

[0052]

Charge Transport Layer

The charge transport layer 37 can be formed by dissolving or dispersing a charge transport material and a binder resin in a proper solvent, applying the dispersant obtained to a charge generating layer, and drying it. Further, to the charge

transport layer 37, one or more kinds of a plasticizer, a leveling agent, an antioxidant, or the like, if necessary, can be added. The charge transport material is a hole transport material or an electronic transport material.

[0053]

Examples of the electronic transport material include, for example, an electron receiving material, such as chloranil, bromanil, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-4H-indeno[1,2-b]thiophen-4-on, 1,3,7-trinitrodibenzothiophen-5,5-dioxide, and a benzoquinone derivative.

[0054]

Examples of the hole transport material include poly-N-vinylcarbazole and a derivative thereof, poly-γ-carbazolylethylglutamate and a derivative thereof, pyrene-formaldehyde condensate and a derivative thereof, polyvinylpyrene, polyvinylphenanthrene, polysilane, an oxazole derivative, an oxadiazole derivative, an imidazole derivative, a monoarylamine derivative, a diarylamine derivative, a triarylamine derivative, a stilbene derivative, an α-phenylstilbene derivative, a benzidine derivative, a diarylmethane derivative, a triarylmethane derivative, a

9-styrylanthracene derivative, a pyrazoline derivative, a divinylbenzene derivative, a hydrazone derivative, an indene derivative, a butadiene derivative, a pyrene derivative, a bisstilbene derivative, an enamine derivative, or the other publicly known materials. The charge transport material can be used alone or in combination.

[0055]

Examples of the binder resin include a thermoplastic or thermosetting resin, such as polystyrene, a styrene-acrylonitrile copolymer, a styrene-butadiene copolymer, a styrene-maleic anhydride copolymer, polyester, polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, polyvinyl acetate, polyvinylidene chloride, a polyallylate resin, a phenoxy resin, polycarbonate, a cellulose acetate resin, an ethyl cellulose resin, polyvinyl butyral, polyvinyl formal, polyvinyl toluene, poly-N-vinylcarbazole, an acryl resin, a silicone resin, an epoxy resin, a melamine resin, a urethane resin, a phenol resin, or an alkyd resin.

[0056]

The amount of the charge transport material is 20 to 300 parts by weight with respect to 100 parts by weight of a binder resin, and preferably 40 to 150 parts by weight. The film thickness of the charge transport layer is preferably 25 μm or less in terms of resolution and respond property. The lower limit value depends on a system (especially a charge potential)

to be used, but is preferably 5 μm or more. Examples of the solvent used in this case include tetrahydrofuran, dioxane, toluene, dichloromethane, monochlorobenzene, dichloroethane, cyclohexanone, methyl ethyl ketone, or acetone. The solvent may be used independently or by mixing two or more kinds.

[0057]

Photosensitive Layer having Single Layer Structure

A case that a photosensitive layer has a single layer structure will be described. For a single photosensitive layer, all of the above charge generating material, charge transport material, the binder resin, and the like can be used. The photosensitive layer can be formed by dissolving or dispersing the charge generating material, the charge transport material, the above sulfur-based compound, and the binder resin in a proper solvent, and coating and drying the dispersion. Further, a plasticizer and a leveling agent can be added if necessary. The amount of the charge generating material is preferably 5 to 40 parts by weight with respect to 100 parts by weight of the binder resin. The amount of the charge transport material is preferably 0 to 190 parts by weight with respect to 100 parts by weight of the binder resin, and more preferably 50 to 150 parts by weight. The photosensitive layer is formed by applying a coating solution by a dip coating method, a spray coat, a bead coat, or a ring coat. The coating solution is made by dispersing the charge generating material, the binder resin, and the charge transport

material with a solvent, such as tetrahydrofuran, dioxane, dichloroethane, or cyclohexane, by a dispersing machine. The film thickness of the photosensitive layer is properly about 5 to 25 μm.

[0058]

(Protective Layer) The protective layer 39 will now be described. The protective layer 39 is formed by dispersing an acryl modified polyorganosiloxane compound, an inorganic filler, and a binder resin in a proper solvent, adding a leveling agent, a charge transport material, or an antioxidant, dissolving those, applying the dispersant obtained to a photosensitive layer, and drying it.

[0059]

Acryl Modified Polyorganosiloxane

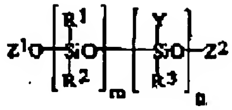
As an acryl modified polyorganosiloxane compound used in this case, a compound having acrylic polymers grafted to main chains of polyorganosiloxane can be used. Particularly, an acryl modified polyorganosiloxane compound having the following composition is preferable.

[0060]

An acryl modified polyorganosiloxane compound prepared by graft polymerization, onto (A) a polyorganosiloxane represented by the general formula (I):

[Chemical Formula 7]

General formula (I)

 ......(I)

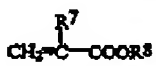
[0061]

(wherein R^1, R^2, R^3, Y, Z^1 and Z^2 are as defined above), of (B) (meth)acrylate represented by the general formula (II):

[0062]

[Chemical Formula 8]

General formula (II)

 .....(II)

[0063]

(wherein, R^7 and R^8 are as defined above) and, if necessary, a copolymerizable monomer.

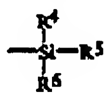
[0064]

In the polyorganosiloxane represented by the general formula (I), R^1, R^2 and R^3 are represent a hydrocarbon group having 1 to 20 carbon atoms, for example, an alkyl group such as a methyl group, an ethyl group, a propyl group, and butyl group, or an aryl group such as a phenyl group, a tolyl group, a xylyl group, and a naphthyl group, and a halogenated hydrocarbon group having 1 to 20 carbon atoms in which at least one of a hydrogen atom bonded with a carbon atom of the hydrocarbon group is replaced by a halogen atom. R^1, R^2 and R^3 may be the same or different. Further, Y represents an organic group having a radical reactive group, such as a vinyl group, an aryl group, a γ-acryloxypropyl group, a γ-methacryloxypropyl group, or a γ-mercaptopropyl group,

a SH group, or both of them. Z^1 and Z^2 represent a lower alkyl group such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, and a butyl group, or a triorganosilyl group represented by the following formula:

[0065]

[Chemical Formula 9]



[0066]

In the triorganosilyl group, R^4 and R^5 are the same or different and each represents a hydrocarbon group having 1 to 20 carbon atoms or halogenated hydrocarbon group, R^6 repents a hydrocarbon group having 1 to 20 carbon atoms or a halogenated hydrocarbon group, or an organic group having a radical reactive group, a SH group or both of them. Examples of the hydrocarbon group having 1 to 20 carbon atoms or halogenated hydrocarbon group, and the organic group having a radical reactive group, a SH group or both of them in the triorganosilyl group include the groups as described above. Z^1 and Z^2 may be the same or different. Further, m is a positive integer of 10,000 or less, preferably from 500 to 8,000, and n is an integer of 1 or more, preferably from 1 to 500.

[0067]

The polyorganosiloxane represented by the general formula (I) can be made by reacting polyorganosiloxane such as, annular

polyorganosiloxane, liquid polydimethylsiloxane in which both ends of a molecular chain is blocked by a hydroxyl group, liquid polydimethylsiloxane in which both ends of a molecular chain is blocked by an alkoxy group, and polydimethylsiloxane in which both ends of a molecular chain is blocked by a trimethylsilyl group, silanes or a hydrolysis product of silanes which are to introduce a radical reactive group, a SH group or both of them, and a trifunctional trialkoxy silane having an amount not to impair the object of the present invention and its hydrolysis product according to necessity.

[0068]

The other production methods of the polyorganosiloxane represented by the general formula (I) will be described. In the first method, polyorganosiloxane having the high molecular weight can be made by using an annular low molecule siloxane, such as octamethylcyclotetrasiloxane, and a dialkoxysilane compound or its hydrolysate having a radical reactive group, a SH group or both of them as raw materials, and polymerizing those under a strong alkali or strong acid catalyst. The polyorganosiloxane prepared by this method is subjected to a treatment to emulsify and disperse in a water-based medium under an existence of a proper emulsifier, in order to carry out the following process of emulsion graft copolymerization.

[0069]

In the second method, polyorganosiloxane is made by using

low molecule polyorganosiloxane, and dialkoxysilane containing a radical reactive group, a SH group or the both of them or its hydrolysate as raw materials, and emulsifying and polymerizing those in a water-based catalyst under the existence of a sulfonic acid-based surfactant agent or a sulfate-based surfactant agent. In the emulsion polymerization, the polymerization can be carried out by using the same materials, and emulsifying and dispersing those in a water-based medium using a cationic surfactant agent such as alkyltrimethyl ammonium chloride or alkylbenzylammonium chloride, adding the proper amount of a strong alkali compound such as potassium hydroxide or sodium hydroxide, and carrying out polymerization.

[0070]

As for the polyorganosiloxane represented by the general formula (I), when the molecular weight is low, an effect to give continuous slidability and abrasion resistance to a formed substance obtained from the component is inferior. Thus, it is desired that the molecular weight is higher as soon as possible. Therefore, in the first method, it is necessary that polyorganosiloxane is made to have a high molecular weight in the polymerization and is emulsified and dispersed. Further, in the second method, when a mature-treatment after the emulsion polymerization is carried out, the molecular weight of polyorganosiloxane becomes large at a low temperature. Thus, the temperature in the aging treatment is 30°C or lower, and

preferably 15°C or lower.

[0071]

In the present invention, Examples of (meth)acrylate represented by the general formula (II) which is used for graft polymerizing onto polyorganosiloxane represented by the general formula (I) as a monomer of the (B) component, include, for example, alkyl (meth)acrylate such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, or stearyl (meth)acrylate, alkoxyalkyl (meth)acrylate such as methoxyethyl (meth)acrylate or butoxyethyl (meth)acrylate, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, and benzyl (meth)acrylate. These (meth)acrylates may be used alone or in combination.

[0072]

Further, polyfunctional monomer or an ethylenically unsaturated monomer can be used according to necessity as a copolymerizable monomer with the (meth)acrylate. Examples of the polyfunctional monomer include, for example, ethylenically unsaturated amide and alkylol or an alkoxyalkylating material of ethylenically unsaturated amide such as (meth)acrylamide, diacetone (meta)acrylamide, N-methylol (meth)acrylamide, N-buthoxymethyl (meth)acrylamide, or N-methoxymethyl

(meth)acrylamide, an oxirane group-containing unsaturated monomer such as glycidyl (meth)acrylate or glycidyl aryl ether, a hydroxyl group-containing unsaturated monomer such as 2-hydroxyethyl (meth)acrylate or 2-hydroxypropyl (meth)acrylate, a carboxyl group-containing ethylenically unsaturated monomer such as (meth)arylic acid, maleic anhydride, crotonic acid, or itaconic acid, an amino group-containing unsaturated monomer such as N-dimethylaminoethyl (meth)acrylate or N-diethylaminoethyl (meth)acrylate, a polyalkylene oxide group-containing unsaturated monomer such as an adduct of ethylene oxide of (meth)acrylic acid or propylene oxide of (meth)acrylic acid, a perfect ester of polyhydric alcohol and (meth)acrylic acid such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, or trimethylolpropane tri(meth)acrylate, acryl (meth)acrylate, or divinylbenzene. These monomers may be used alone or in combination. These polyfunctional monomers have an effect to give elasticity, durability and heat resistance to a formed substance by relating to bridge between polymers in an acryl modified polyorganosiloxane.

[0073]

In contrast, examples of the ethylenically unsaturated monomer include, for example, styrene, α-methylstyrene, vinyltoluene, acrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl propionate, or vinyl versatate.

These monomers may be used alone or in combination. Further, one or more kinds of the monomer may be used in combination with one or more kinds of the polyfunctional monomers. The using amount of the copolymerizable monomer used according to necessity is necessarily within the range of 30% by weight or less based on the total weight of (meth)acrylate represented by the general formula (II) and the copolymerizable monomer. When the amount is more than 30% by weight, mixing property of an acryl modified polyorganosiloxane and a binder resin decreases.

[0074]

Further, as for the graft copolymerizable monomer of the (B) component, that is, (meth)acrylate represented by the general formula (II) or a mixture of the (meth)acrylate and the copolymerizable monomer, in order to give more excellent slidability and abrasion resistance to a molded substance, a glass transition temperature is 20°C, and preferably 30°C or more. An acryl modified polyorganosiloxane in the present invention can be obtained by using polyorganosiloxane of the component (A) and a monomer of the component (B) in a weight ratio of 5:95 to 95:5 and graft-copolymerizing those by an emulsion polymerization method.

[0075]

When the using ratio of polyorganosiloxane of the (A) component is less than the above range, an acryl modified polyorganosiloxane cannot fully exert the effect of the

polyorganosiloxane itself, and adhesion which is a fault of an acryl-based polymer generates. Further, when the ratio is more than the above range, mixing property of the acryl modified polyorganosiloxane with a polyvinyl chloride-based resin decreases, and thus the acryl modified polyorganosiloxane is easily bled toward the surface of a formed substance. Thus, slidability or abrasion resistance may temporarily decrease.

[0076]

The emulsion graft copolymerization of the (A) and (B) components can be carried out by a publicly known emulsion polymerization method using water-based emulsion of polyorganosiloxane as the component (A) and a conventional radical initiator. In addition, a production method of an acryl modified polyorganosiloxane is concretely described in pages 4 to 8 of Japanese Examined Patent Publication No. H7-5808 (Nissin Chemical Industry Co., Ltd.) and specific production examples are described in pages 9 to 10 of Japanese Examined Patent Publication No. H7-5808.

[0077]

Further, in the acryl modified polyorganosiloxane used in the present invention, residual impurities of an emulsifier and a flocculant which are used at the time of polymerization may damage electrical property of an image forming member, being an important problem for electrical property, especially in an electrophotographic photoreceptor. Thus, the acryl modified

polyorganosiloxane are preferably refined if necessary. A refining method is a method of carrying out a stirring and washing treatment using an acid or alkali aqueous solution, water and alcohol, or a method of extracting a solid-liquid by Soxhlet extraction. The ratio of the modified polyorganosiloxane in the protective layer is 40% or less by weight, and more preferably 20% or less by weight. When the ratio is 40% or more by weight, smoothing property of the surface of a photoreceptor decreases, and side effect such as increasing residual potential is caused.

[0078]

Further, a method of adding a modified polyorganosiloxane to a resin is a method of stirring the polyorganosiloxane in a general solvent, a ball milling method, a vibration milling method or a supersonic method. Alternatively, a method of mechanically mixing the polyorganosiloxane using a publicly known apparatus, such as a Banbury mixer, a roll mill or a twin-screw extruder, and shaping it in a pellet form, can be used. The extruded and shaped pellet can be molded within a wide temperature range, and a conventional injection molding machine is used for molding. A graft copolymer having the acryl modified polyorganosiloxane shaped in a pellet form and a resin can be applied for the above solution dispersing method. A typical example of the modified polyorganosiloxane used in the present invention is one marketed having a product name of CHALINE R-170S, R-170 or R-210 manufactured by Nissin Chemical Industry

Co., Ltd.

[0079]

Examples of a material of the binder resin used for the protective layer 39 include an ABS resin, an ACS resin, an olefin-vinyl monomer copolymer, chlorination polyether, an aryl resin, a phenol resin, polyacetal, polyamide, polyamideimide, polyacrylate, polyarylsulfone, polybutylene, polybutylene terephthalate, polycarbonate, polyethersulfone, polyethylene, polyethylene terephthalate, polyimide, an acryl resin, polymethylpentene, polypropylene, polyphenyl oxide, polysulfone, polystyrene, polyallylate, an AS resin, a butadiene-styrene copolymer, polyurethane, polyvinyl chloride, polyvinylidene chloride, or an epoxy resin. Particularly, polycarbonate or polyallylate is effective from the points of dispersibility of a filler, residual potential and coated film defects.

[0080]

Inorganic Filler

Examples of a material of the inorganic filler used in the present invention include a powderof a metal such as copper, tin, aluminum, or indium, a metal oxide such as silica, tin oxide, zinc oxide, titanium oxide, alumina, zirconium oxide, indium oxide, antimony oxide, bismuth oxide, calcium oxide, tin oxide doped with antimony, or indium oxide doped with tin, a metal fluoride, such as tin fluoride, calcium fluoride, or aluminum

fluoride, potassium titanate, or boron nitride. In the filler, an inorganic pigment as an inorganic filler is effectively used to improve abrasion resistance from the points of the hardness of the filler.

[0081]

Further, the inorganic filler can be subjected to a surface treatment using at least one kind of a surface treating agent. The surface treatment is preferable from the points of dispersibility of an inorganic filler. As decreasing of dispersibility of an inorganic filler, a residual potential increase. In addition, the decreasing of dispersibility causes decreasing transparency of a coated film, the defect generation in a coated film, and decreasing of abrasion resistance. Thus, decreasing of the dispersibility may cause many problems to prevent making high durability and high image quality. As for the surface treating agent, any one of conventionally used surface treating agent can be used, but a surface treating agent capable of maintaining insulation of an inorganic filler is preferable.

[0082]

For example, a titanate-based coupling agent, an aluminum-based coupling agent, a zircoaluminate-based coupling agent, a higher fatty acid, or mixing treatment of a silane coupling agent with these agents, or Al_2O_3, TiO_2, ZrO_2, silicone, aluminum stearate, or the like and mixing treatment of them can

be preferably used. These agents are more preferable from the points of dispersibility of an inorganic filler and an image blur. A treatment with a silane coupling agent causes a strong influence of an image blur. However, when the silane coupling agent is subjected to a mixing treatment with the above surface treating agent, the influence may be suppressed. An amount of the surface treatment depends on an average primary particle size of an inorganic filler to be used, but is preferably 3 to 30% by weight, and more preferably 5 to 20% by weight. When the amount of the surface treatment is less than the above amount, the effect to disperse the inorganic filler cannot be obtained, and when the amount is too high, remarkably increasing of residual potential is caused.

[0083]

As the solvent to be used, any one of all solvents used in the charge transport layer 37, such as tetrahydrofuran, dioxane, toluene, dichloromethane, monochlorobenzene, dichloroethane, cyclohexanone, methyl ethyl ketone, or acetone can be used. However, a solvent having high viscosity is proper at the time of dispersing, and a solvent having high volatility is proper at the time of coating. When there are no solvents to satisfy these above conditions, two or more kinds of solvents respectively having viscosity and volatility can be mixed to be used. The solvent may have a large effect with respect to dispersibility and residual potential of the filler.

[0084]

Further, the addition of the charge transport material, which is described in the description of the charge transport layer 37, to the protective layer is effective and is useful to decrease residual potential and improve image quality. At this time, when a charge transport material is added to the protective layer, in which an ionization potential (Ip) of a charge transport material contained in a protective layer is equal to or smaller than the Ip of a charge transport material contained in a photosensitive layer, charge injecting property to the protective layer is improved. Thus, the effect to decrease residual potential more can be obtained. In addition, the ionization potential can be measured by various methods such as a spectroscopically measuring method and an electrochemically measuring method.

[0085]

The material of the inorganic filler can be dispersed by a conventional method such as a ball mill, an attriter, a sand mill or a supersonic wave. In these methods, the ball mill is more preferable from the points of dispersibility, since impurities are hardly mixed from an external. A material of a media used in the ball mill can be all conventionally used media, such as zirconia, alumina and agate.

[0086]

Further, an average primary particle diameter of the

inorganic filler is preferably 0.01 to 0.6 μm from the points of light transmittance and abrasion resistance of the protective layer. When the average primary particle size of the inorganic filler is 0.01 μm or less, decreasing abrasion resistance or decreasing dispersibility is caused. When the diameter is 0.6 μm or more, precipitation of the inorganic filler may be advanced, and filming of a toner may be caused.

[0087]

Method for Forming Protective Layer

As a method for forming a protective layer, conventional methods such as a dip coating method, a spray coating method, a bead coating method, a nozzle coating method, a spinner coating method, or a ring coating method can be used. However, particularly, the spray coating method is more preferable from the points of uniformity of a coated film. Further, a protective layer can be formed by coating a protective layer one time to be the needed film thickness. However, when a protective layer can be a multiple layer by coating two or more times, it is more preferable from the points of uniformity of the filler in the film. Accordingly, the effect to more decrease residual potential, improving resolution, and improving abrasion resistance can be obtained. In addition, the thickness of the protective layer is suitably about 0.1 to 10 μm.

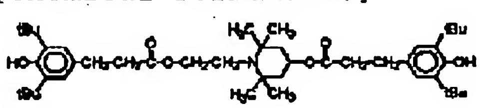
[0088]

Other Additional Components

The protective layer can be added with an organic filler in addition to the acryl modified polyorganosiloxane compound and the inorganic filler. Examples of a material of the organic filler include a fluoro resin powder such as polytetrafluoroethylene, a silicone resin powder, or a-carbon powders. Further, to the protective layer, a leveling agent such as silicone oil, an antioxidant described below, and a dispersing material of the filler can be added. The antioxidant can be conventionally, publicly known ones. For example, a compound having both of a hindered amine structure and a hindered phenol structure, which are described below, can be used.

[0089]

[Chemical Formula:10]



[0090]

A dispersant of the filler used in the present invention can be publicly known dispersants. Particularly, an organic compound having a structure containing at least one carboxyl group in a polymer or a copolymer is preferable. A polycarboxylic acid derivative is preferable from the point of dispersibility. A carboxylic acid part in the dispersant is to give acid value and important to improve dispersibility. A hydrophilic inorganic filler has low affinity with an organic solvent or a binder resin, and thus the filler cannot be sufficiently

dispersed by using any dispersing methods when dispersing as it is.

[0091]

However, the dispersant in the present invention has high affinity with the inorganic filler at the carboxylic acid part. The other polymer part has high affinity with a binder resin or an organic solvent. Thus, affinity of the inorganic filler with an organic solvent or a binder resin can increase through a dispersant. Further, an acid value of these dispersants is preferably 10 to 400 mgKOH/g, and more preferably 30 to 200 mgKOH/g. When the acid value is too high, an image is influenced, e.g., resolution decreases. When the acid value is too low, it is necessary to increase the additional amount of the dispersants, and electrical properties may easily decrease.

[0092]

(Under Coating Layer) In a photoreceptor of the present invention, an under coating layer can be formed between the conductive support 31 and the photosensitive layer. The under coating layer mainly, generally contains a resin. However, when it is considered that the resin is coated with a photosensitive layer with a solvent, a resin having high solvent resistance with respect to a general organic solvent is desirable. Examples of the resin include a curing type resin having a three-dimensional mesh structure, e.g., a water soluble resin such as polyvinyl alcohol, casein, or sodium polyacrylate, an

alcoholic soluble resin such as copolymerization nylon, or methoxymethylated nylon, polyurethane, a melamine resin, a phenol resin, an alkyd-melamine resin, and an epoxy resin. Further, the under coating layer can be added with a fine powdered pigment of a metal oxide such as titanium oxide, silica, alumina, zirconium oxide, tin oxide, indium oxide in order to prevent moire and reduce residual potential.

[0093]

The under coating layer can be formed by using a proper solvent and a coating method like the above photosensitive layer. The under coating layer of the present invention can be formed using a silane coupling agent, a titanium coupling agent, or a chromium coupling agent. In addition, the under coating layer can be preferably a layer containing Al_2O_3 coated by anodic-oxidizing, or a layer containing an organic material such as polyparaxylene (parylene) or an inorganic material such as SiO_2, SnO_2, TiO_2, ITO or CeO_2, which are made by a vacuum thin film coating method. In addition to those, publicly known layers can be used. The film thickness of the under coating layer is properly 0 to 5 μm.

[0094]

(Electrophotographic Method/Electrophotographic Apparatus) An electrophotographic method and an electrophotographic apparatus of the present invention will now be described in detail with reference to the accompanying

drawings.

[0095]

FIG. 4 is a schematic view for explaining an electrophotographic process and an electrophotographic apparatus, and the following examples are contained in the present invention. In FIG. 4, a photoreceptor 1 has a drum shape, but may have a sheet shape or an endless belt shape. An electrification charger 3, a pre-transfer charger 7, a transfer charger 10, a separation charger 11, and a pre-cleaning charger 13, a corotron, a scorotron, solid electrification machine (a solid state charger), an electrification roller are used. All known means can be used. As the transfer means, the above general charger can be used, but a charger containing a transfer charger and a separation charger illustrated in FIG. 4 is effective.

[0096]

Further, as light sources such as an image exposing portion 5 and a diselectrification lamp 2, general emitting products such as a fluorescent light, a tungsten lamp, a halogen lamp, a mercury lamp, a sodium-vapor lamp, a light emitting diode (LED), a semiconductor laser (LD), and electroluminescence (EL) can be used. In order to irradiate only light having a desired wavelength band, various filters such as a sharp cut filter, a band path filter, a near-infrared cut filter, a dichroic filter, an interference filter, and a filter for converting color and temperature can be used. In the light sources, a transfer process,

a diselectrification process, a cleaning process, and a pre-exposing process are provided using light irradiating in addition to the processes illustrated in FIG. 4. By these processes, light is irradiated to a photoreceptor.

[0097]

Toners developed on the photoreceptor 1 by a developing unit 6 are transferred to a transfer paper 9, but all toners are not transferred. There are residual toners on the photoreceptor 1. The residual toners are removed from the photoreceptor by a fur brush 14 and a blade 15. Cleaning is carried out by only a cleaning brush, and the cleaning brush can be publicly known ones such as a fur brush and a magfur brush. When an electrophotography photoreceptor is subjected to positive (negative) charging to carry out image exposing, a positive (negative) electrostatic latent image is formed on the surface of a photoreceptor. When the electrostatic latent image is developed by negative (positive) electrode toners (voltage detection fine particles), a positive (negative) image can be formed. When the image is developed by positive (negative) electrode toners, a negative image can be formed. These developing means can be a publicly known method, and the diselectrification means can be a publicly known method.

[0098]

FIG. 5 shows another example of an electrophotographic process of the present invention. A photoreceptor 21 is driven

by a driving rollers 22a and 22b, and charging by a charger 23, image exposing by a light source 24, developing (not shown), transferring by a transfer charger 25, a pre-cleaning exposing by a light source 26, cleaning by a cleaning brush 27, and diselectrification by a light source 28 are repeatedly carried out. In FIG. 5, light irradiation of pre-cleaning exposing is carried out to the photoreceptor 21 from the support side (of course, a support is translucent in this case).

[0099]

The electrophotographic process illustrated in the drawings indicates an embodiment of the present invention and, of course, the present invention can be applied to the other embodiments. For example, in FIG. 5, pre-cleaning exposing is carried out from the support side. However, the exposing can be carried out from the photosensitive layer side. Further, irradiation of image exposing and diselectrification light can be carried out from the support side. On the other hand, as for light irradiating processes, image exposing, pre-cleaning exposing, and diselectrification exposing are illustrated in the drawings. However, in addition to the processes, pre-transfer exposing, pre-exposing of image exposing, and the other publicly known light irradiating processes can be provided so as to irradiate light to the photoreceptor.

[0100]

The image forming means described above can be provided

fixing in a copying machine, a facsimile or a printer, but can be provided in the state of a process cartridge in the apparatuses. The process cartridge is one apparatus (components) internally containing a photoreceptor, charging means, exposing means, a developing means, transfer means, cleaning means, and diselectrification means. The process cartridge can generally have many shapes, but a typical example of the shape is illustrated in FIG. 6.

[0101]

[Examples]

The present invention will now be described by way of examples, but the present invention is not limited by the following examples. In addition, all parts means parts by weight.

[0102]

[Example 1]

A under coating layer having a thickness of 3.5 μm, a charge generating layer having a thickness of 0.2 μm, and a charge transport layer having a thickness of 20 μm were formed by sequentially applying a coating solution for an under coating layer, a coating solution for a charge generating layer, and a coating solution for a charge transport layer , which have the following compositions, to an aluminum cylinder by a dip coating, and drying. These liquids had the following compositions.

[0103]

<Coating Solution for Under Coating Layer>

Titanium-dioxide powder: 400 parts

Melamine resin: 40 parts

Alkyd resin: 60 parts

2-butanone: 500 parts

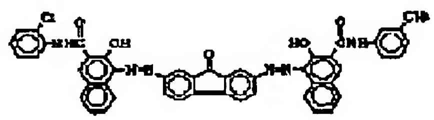
[0104]

<Coating Solution for Charge Generating Layer>

Bisazo pigment having the following structure: 12 parts

[0105]

[Chemical Formula 11]



[0106]

Polyvinylbutyral: 5 parts

2-butanone: 200 parts

Cyclohexanone: 400 parts

[0107]

<Coating Solution for Charge Transport Layer>

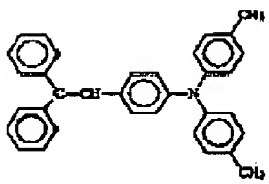
Polycarbonate (Z POLYCA, Teijin Chemicals Ltd.): 10 parts

Charge transport material having the following structural formula: 10 parts

[0108]

[Chemical Formula 12]

PAGE 74/102 * RCVD AT 9/12/2007 9:13:14 PM [Eastern Daylight Time] * SVR:USPTO-EFXRF-6/1 * DNIS:2738300 * CSID:651 699 7901 * DURATION (mm-ss):11-04



[0109]

Tetrahydrofuran: 100 parts

1% Silicone oil (KF50-100CS, Shin-Etsu Chemical Co., Ltd.) in tetrahydrofuran solution: 1 part

[0110]

A protective layer having a thickness of about 5 μm was formed by applying a protective layer coating solution having the following composition, which was made by ball milling, on the charge transport layer by a ring coating. Then, an electrophotographic photoreceptor of Example 1 was made. A part of the made photoreceptor was peeled and the dispersing state of an acryl modified polyorganosiloxane was observed by a sectional TEM of the protective layer. Then, it was confirmed that a particle dispersing film having a thickness of about 0.1 to 4 μm was formed. Further, as for a liquid made by dissolving and dispersing CHALINE R-170S, which was used for the protective layer coating solution, in tetrahydrofuran, aggregates were lost by dissolving but particles which has a size equal to the primary particle or less were not dissolved. The liquid was not quite passed through a filter of 0.2 μm due to swelling. Accordingly, it was confirmed that CHALINE R-170S in the protective layer was in a micro gel state.

[0111]

<Coating Solution for Protective Layer>

Acryl modified polyorganosiloxane: 0.6 parts

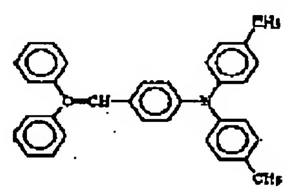
(CHALINE R-170S, which was acryl modified polyorganosiloxane compound, manufactured by Nissin Chemical Industry Co., Ltd., average primary particle size: 0.2 μm, an average particle size: 30 μm, including 70% of an organopolysiloxane component and 30% of an acryl component)

Alumina (having average primary particle size: 0.3 μm, manufactured by Sumitomo Chemical Co., Ltd.): 1.1 parts

Charge transport material having the following structural formula (Ip: 5.4eV): 4 parts

[0112]

[Chemical Formula 13]



[0113]

Polycarbonate (Z POLYCA, Teijin Chemicals Ltd.): 5.5 parts

Dispersant BYK-P104 (BYK Corporation): 0.1 parts

Tetrahydrofuran: 220 parts

Cyclohexanone: 80 parts

Vibration mill dispersing: 60 minutes

[0114]

[Example 2]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that CHALINE R-170 (Acryl modified polyorganosiloxane compound manufactured by Nissin Chemical Industry Co., Ltd., an average primary particle size: 0.2 µm, average particle size: 350 µm, including 70% of an organopolysiloxane component and 30% of an acryl component) was used as an acryl modified polyorganosiloxane for a protective layer. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were the same as in Example 1.

[0115]

[Example 3] An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that CHALINE R-210 (Acryl modified polyorganosiloxane compound manufactured by Nissin Chemical Industry Co., Ltd., average primary particle size: 0.2 µm, average particle size: 350 µm, including 10% of an organopolysiloxane component and 90% of an acryl component) was used as an acryl modified polyorganosiloxane for a protective layer. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

[0116]

[Example 4]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that an inorganic filler

contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Titanium oxide (having an average primary particle size of 0.3 μm, manufactured by Ishihara Sangyo Kaisha Ltd.): 1.1 parts

[0117]

[Example 5]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that an inorganic filler contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Alumina (average primary particle size: 0.6 μm, manufactured by Ishihara Sangyo Kaisha Ltd.): 1.1 parts

[0118]

[Example 6]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that an inorganic filler contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Silica (average particle size: 0.015 μm, manufactured by

Shin-Etsu Silicones Corporation): 0.8 parts

[0119]

[Example 7]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that an inorganic filler contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Surface treated alumina with a titanate-based coupling agent: 1.1 parts

(Surface treated alumina made by subjecting 10 parts of alumina (having an average primary particle size of 0.3 μm, manufactured by Sumitomo Chemical Co., Ltd.) with 1 part of PLENACT KR TTS (manufactured by Ajinomoto Fine-Techno. Co. Inc) which is a titanate-based coupling agent)

[0120]

[Example 8]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that an inorganic filler contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Surface treated alumina with an aluminum-based coupling agent:

1.1 parts

(Surface treated alumina made by subjecting 10 parts of alumina (having an average primary particle size of 0.3 µm, manufactured by Sumitomo Chemical Co., Ltd.) with 1 part of PLENACT AL-M (manufactured by Ajinomoto Fine-Techno. Co. Inc) which is an aluminum-based coupling agent)

[0121]

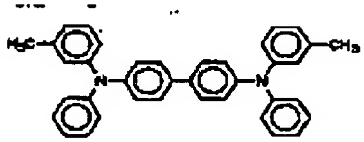
[Example 9]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that a charge transport material contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Charge transport material having the following structural formula: 10 parts

[0122]

[Chemical Formula 14]



[0123]

[Example 10]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that a charge transport material contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

same manner as in Example 1, except that a protective layer did not contain a charge transport material and a film thickness of the protective layer was 2 μm. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

[0124]

[Example 11]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that a binder resin contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Polyallylate resin (U POLYMER, manufactured by UNITIKA LTD.): 10 parts

[0125]

[Example 12]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that a binder resin contained in a protective layer was changed to the following material. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

Polystyrene resin: 10 parts

[0126]

[Example 13]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that a coating solution for a charge generating layer, a coating solution for a charge transport layer, and a coating solution for a protective layer were changed to the following materials. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

[0127]

<Coating solution for Charge Generating Layer>

Y-typed titanyl phthalocyanine: 9 parts

Polyvinylbutyral: 5 parts

2-butanone: 450 parts

[0128]

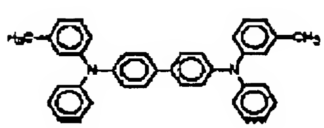
<Coating solution for Charge Transport Layer>

C-typed polycarbonate: 10 parts

Charge transport material having the following structure: 8 parts

[0129]

[Chemical Formula 15]



[0130]

Organic sulfur based compound having the following structural

formula (manufactured by Sumitomo Chemical Co., Ltd.): 0.15 parts

[0131]

[Chemical Formula 16]

$S \leftarrow CH_2CH_2COOC_{14}H_{29})_2$

[0132]

Toluene: 70 parts

[0133]

< Coating solution for Protective Layer>

Acryl modified polyorganosiloxane (CHALINE R-170S, which is an acryl modified polyorganosiloxane compound, manufactured by Nissin Chemical Industry Co., Ltd., average primary particle size: 0.2 μm, average particle size: 30 μm, including 70% of an organopolysiloxane component and 30% of an acryl component): 0.6 parts

Alumina-treated titanium oxide (having an average primary particle size of 0.035 μm, manufactured by TAYCA Corporation): 1.2 parts

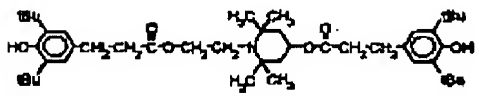
Methacrylic acid-methyl methacrylate copolymer (having an acid value of 50 mgKOH/g): 0.5 parts

C-typed polycarbonate (manufactured by Teijin Chemicals Ltd.): 5.5 parts

Compound having a hindered amine structure and a hindered phenol structure, which has the following structural formula: 0.24 parts

[0134]

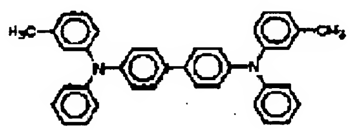
[Chemical Formula 17]



Charge transport material (Ip: 5.3 eV) having the following structural formula: 4 parts

[0135]

[Chemical Formula 18]



[0136]

Tetrahydrofuran:	250 parts
Cyclohexanone:	50 parts
Vibration mill:	60 minutes

[0137]

[Example 14]

An electrophotographic photoreceptor was produced in the same manner as in Example 10, except that CHALINE R-210 (Acryl modified polyorganosiloxane compound manufactured by Nissin Chemical Industry Co., Ltd., average primary particle size: 0.2 μm, particle size: 350 μm, including 10% of an organopolysiloxane component and 90% of an acryl component) was used as an acryl modified polyorganosiloxane for a protective layer. Further, when a dispersing state of the acryl modified polyorganosiloxane was observed by the same method as in Example 1. Consequently, the results were same as in Example 1.

[0138]

[Comparative Example 1]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that a protective layer was not formed.

[0139]

[Comparative Example 2]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that alumina was not added to a coating solution for a protective layer.

[0140]

[Comparative Example 3]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0141]

[Comparative Example 4]

An electrophotographic photoreceptor was produced in the same manner as in Example 2, except that alumina was not added to a coating solution for a protective layer.

[0142]

[Comparative Example 5]

An electrophotographic photoreceptor was produced in the same manner as in Example 3, except that alumina was not added to a coating solution for a protective layer.

[0143]

[Comparative Example 6]

An electrophotographic photoreceptor was produced in the same manner as in Example 4, except that an acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0144]

[Comparative Example 7]

An electrophotographic photoreceptor was produced in the same manner as in Example 5, except that acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0145]

[Comparative Example 8]

An electrophotographic photoreceptor was produced in the same manner as in Example 6, except that acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0146]

[Comparative Example 9]

An electrophotographic photoreceptor was produced in the same manner as in Example 7, except that an acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0147]

[Comparative Example 10]

An electrophotographic photoreceptor was produced in the same manner as in Example 8, except that an acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0148]

[Comparative Example 11]

An electrophotographic photoreceptor was produced in the same manner as in Example 13, except that a protective layer was not formed.

[0149]

[Comparative Example 12]

An electrophotographic photoreceptor was produced in the same manner as in Example 13, except that an aluminum-treated titanium oxide was not added to a coating solution for a protective layer.

[0150]

[Comparative Example 13]

An electrophotographic photoreceptor was produced in the same manner as in Example 13, except that an acryl modified polyorganosiloxane was not added to a coating solution for a protective layer.

[0151]

[Comparative Example 14]

An electrophotographic photoreceptor was produced in the same manner as in Example 13, except that an aluminum-treated titanium oxide was not added to a coating solution for a protective layer.

same manner as in Example 1, except that the following material was added to a coating solution for a protective layer instead of an acryl modified polyorganosiloxane.

Silicon fine particle (Tospearl 105 manufactured by GE Toshiba Silicones, average particle size: 0.5 μm)

[0152]

[Comparative Example 15]

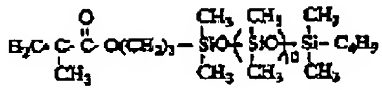
An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that the following material was added to a coating solution for a protective layer instead of an acryl modified polyorganosiloxane. Acryl-silicone based graft polymer (SYMAC US-450 manufactured by TOAGOSEI CO., LTD., made by extracting only a solid content from an aqueous emulsion having a 30% solid content)

[0153]

[Comparative Example 16]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that the following material was added to a coating solution for a protective layer instead of an acryl modified polyorganosiloxane. A silicon graft polyacryl resin made by polymerizing 30 parts of dimethylsiloxane having methacryloxy at one side terminal and 70 parts of methyl methacrylate in toluene/aqueous emulsion using azobisisobutyronitrile as a radical reactive initiator.

[Chemical Formula 19]



[0154]

[Comparative Example 17]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that the following material was added to a coating solution for a protective layer instead of an acryl modified polyorganosiloxane.

Alkoxy modified silicone (KF-851, manufactured by Shin-Etsu Silicones Corporation)

[0155]

[Comparative Example 18]

An electrophotographic photoreceptor was produced in the same manner as in Example 1, except that the following material was added to a coating solution for a protective layer instead of an acryl modified polyorganosiloxane.

Spherical melamine particles (EPOSTAR S manufactured by NIPPON SYOKUBAI Corporation, primary particle size: 0.3 μm)

[0156]

The electrophotographic photoreceptors of Examples 1 to 14 and the electrophotographic photoreceptors of Comparative Examples 1 to 18 were installed in Imagio MF6550 which is a digital copying machine made by RICOH Corporation, or a modified machine of Imagio MF6550 (having a laser wavelength of a light source for writing of 655 nm). Then, 50,000 sheets were continuously

printed. Then, images were formed under the conditions that temperature was 25°C and humidity was 90%, and dark portion potential, bright portion potential, and image quality were evaluated. The dark portion potential, bright portion potential and image quality were evaluated as follows.

[0157]

Dark portion potential: A surface potential of a photoreceptor when the photoreceptor transfers to the position of a developing portion after primary charging.

Bright portion potential: The surface potential of the photoreceptor when the receptor receives image exposing (overall exposure) and transfers to the position of the developing portion after primary charging

Image quality: Total evaluation of image density, fine-line reproducibility, image blurring, resolution, and background stains about an outputted image.

Further, after 50,000 sheets were printed, a film thickness was measured, and the abrasion amount was evaluated by the difference in film thickness before and after printing. These results were shown in Table 1.

[0158]

[Table 1]

	Initial stage			After printing 50,000 sheets			
	Dark portion potential	Bright portion potential	Image quality	Dark portion potential	Bright portion potential	Image quality	Abrasion amount
Example 1	800	90	Good	810	105	Good	0.8
Example 2	800	95	Good	790	105	Good	0.8
Example 3	800	100	Good	800	100	Resolution slightly decreased	0.9
Example 4	810	100	Good	800	105	Good	0.7
Example 5	810	95	Good	820	100	Good	0.8
Example 6	790	90	Good	820	90	Good	0.8
Example 7	800	90	Good	810	95	Good	0.8
Example 8	810	95	Good	800	100	Good	0.8
Example 9	810	100	Good	800	110	Good	0.8
Example 10	820	140	Good	820	220	Image density slightly decreased	0.7
Example 11	800	95	Good	800	110	Good	1.2
Example 12	800	90	Good	800	50	Slight background stains occurred	4.0
Example 13	790	110	Good	800	120	Good	0.8
Example 14	790	120	Good	810	130	Resolution slightly decreased	0.8
Comparative Example 1	800	50	Good	500	45	Background stains occurred on the whole surface	8.5
Comparative	800	60	Good	700	85	Background	8.0

Example 2						stains occurred on the whole surface	
Comparative Example 3	800	95	Good	800	160		1.0
Comparative Example 4	800	60	Good	700	60	Background stains occurred on the whole surface	8.0
Comparative Example 5	800	65	Good	700	55	Background stains occurred on the whole surface	8.0
Comparative Example 6	810	90	Good	800	180	Image flow occurred by filming	0.8
Comparative Example 7	810	95	Good	810	180	Image flow occurred by filming	1.0
Comparative Example 8	800	80	Good	800	150	Image flow occurred by filming	1.0
Comparative Example 9	810	90	Good	800	180	Image flow occurred by filming	1.0
Comparative Example 10	810	80	Good	810	170	Image flow occurred by filming	1.0
Comparative Example 11	800	50	Good	450	60	Background stains occurred on the whole surface	10.0
Comparative	800	60	Good	500	40	Background	9.0

Example 12						stains occurred on the whole surface	
Comparative Example 13	800	100	Good	800	140	Image flow occurred by filming	1.0
Comparative Example 14	800	100	Good	800	140	Image flow occurred by filming	0.8
Comparative Example 15	800	105	Good	810	160	Image flow occurred by filming	0.9
Comparative Example 16	800	100	Good	805	160	Image flow occurred by filming	0.9
Comparative Example 17	810	120	Good	815	260	Image flow occurred by filming	0.8
Comparative Example 18	810	110	Good	800	150	Image flow occurred by filming	0.8

[0159]

As is apparent from the results of the evaluations shown in Table 1, when a photoreceptor does not contain a protective layer, a film scraping amount is high, and background stains due to charge leak occurred on the whole surface when about 50,000 sheets were printed, and then the lifetime of the photoreceptor had ended. Further, in a case of containing only an inorganic filler in a protective layer, abrasion resistance was remarkably improved, but cleaning property deteriorates. Filming of a toner material and a developer component generated on a photoreceptor. Thus, image flow generated under a condition of high humidity. (In this case, the image flow is the following phenomenon. That is, when a charge latent image is formed on a photoreceptor, a part of the photoreceptor, in which a material is adhered on the surface of the photoreceptor by filming, is in a state of low electric resistance by the material and moisture absorbed in the material. Thus, the charge is scattered in the direction to the photoreceptor. As a result, an image after developing is not formed or the shape of the image is changed like flowing.) Further, when only acryl modified polyorganosiloxane was contained in a protective layer, background stains due to abrasion generated like the case of not having a protective layer, and the lifetime was short. In contrast, the photoreceptor of the present invention containing both of acryl modified polyorganosiloxane and an inorganic filler

in a protective layer had abrasion resistance and cleaning property, and could output high quality image for a long period under the condition of high humidity.

[0160]

Further, in a case of containing both of acryl modified polyorganosiloxane and an inorganic filler in a protective layer, when the weight of polyorganosiloxane was higher than the weight of the (meth)acrylate or a mixture of (meth)acrylate of 70 % or more by weight and a copolymerizable monomer of 30% or less by weight, the resolution is hardly reduced, and thus image stability was particularly excellent.

[0161]

Further, in a case of containing both of acryl modified polyorganosiloxane and an inorganic filler in a protective layer, when a charge transport material was contained in the protective layer, potential was hardly varied, and image density was hardly reduced. Thus, image stability was particularly excellent.

[0162]

Further, in a case of containing both of acryl modified polyorganosiloxane and an inorganic filler in a protective layer, when a polycarbonate resin or a polyacrylate resin was used for the protective layer, the abrasion resistance of the protective layer was high, background stains due to film scrapping hardly generated, and thus image stability was particularly excellent. Further, when a silicon fine particle or a silicon graft acryl

resin was added instead of acryl modified polyorganosiloxane, the cleaning property after repeatedly printing was not sufficiently continued, and the image flow due to filming generated. Thus, the similar effect of a polycarbonate resin and a polyacrylate resin could not be obtained. Furthermore, when an inorganic filler and a general organic filler were mixed, there was no effect to improve the cleaning property, and the image flow due to filming generated.

[0163]

[Effect of the Invention]

As described above, when an electrophotographic photoreceptor contains a protective layer containing an inorganic filler and an acryl modified polyorganosiloxane compound in the protective layer, the electrophotographic photoreceptor can have excellent abrasion resistance, smoothing property and foreign substance removing property. Therefore, an abnormal image such as image void or image flow is hardly formed. Such an abnormal image is caused by background stains caused from a pin hall and insufficient cleaning, and the adhesion of a foreign substance. The pin hole is made by discharge breakdown which is generated by decreasing a film thickness due to abrasion. Thus, an electrophotographic photoreceptor capable of outputting a stable image for a long period can be provided.

[0164]

Further, a compound having an acrylic polymer grafted on a silicone main chain is used for the acryl modified polyorganosiloxane compound to be used, and specific emulsion grafted copolymers represented by the general formulas (A) and (B) are used for the acryl modified polyorganosiloxane compound to be used. Thus, the electrophotographic photoreceptor capable of outputting a stable image for a long period can be provided.

[0165]

Further, when the weight of a polyorganosiloxane part is higher than that of an acryl polymerized , smoothing property and foreign matter removing property are excellent, and durability of those is excellent. Thus, a more stable image can be outputted.

[0166]

Further, when the acryl modified polyorganosiloxane compound is granularly dispersed in a protective layer, it becomes possible to have abrasion resistance and smoothing property with durability foreign matter removing property in the well balance. Compatibility of these properties is hard in the conventional technique. Furthermore, when the acryl modified polyorganosiloxane compound is in the form of a micro gel, the particle dispersed compound can be easily formed. Thus, it is possible to provide an electrophotographic photoreceptor which has excellent abrasion resistance and forms a stable image

when repeatedly used at a low cost.

[0167]

Further, when an inorganic filler containing at least one kind of a metal oxide is used, a photoreceptor capable of having remarkably low abrasion amounts, preventing an abnormal image such as background stains due to abrasion can be provided. The photoreceptor can maintain high image quality for long period, and has long lifetime. Further, when a metal oxide subjected to a surface treatment with a surface treating agent is used, the dispersibility of the inorganic filler is improved. As a result, a coating solution becomes stable and it is possible to produce a photoreceptor having no coated film defects in which the filler is uniformly dispersed. Thus, a photoreceptor having high image quality, excellent mechanical strength, and abrasion resistance can be provided while maintaining a low frictional coefficient.

[0168]

Further, when a charge transport material is contained in a protective layer, charge transfer is sufficient, sensitivity is improved, a residual potential is reduced, a difference between dark portion potential and bright portion potential can be sufficiently kept. Thus, a photoreceptor capable of outputting an image in high speed, outputting a high quality image, and outputting an image with high stability can be provided. Furthermore, when a polycarbonate resin and/or a polyallylate

resin are used as a binder resin in a protective layer, a photoreceptor having high maintaining property of the inorganic filler and excellent mechanical strength can be provided even when an acryl modified polyorganosiloxane compound is added. The photoreceptor can have excellent mechanical strength and abrasion resistance, and can maintain a low frictional coefficient.

[0169]

As for an electrophotographic method, an electrophotographic apparatus and a process cartridge, which use the electrophotographic photoreceptor, it is not necessary to exchange a photoreceptor for a long period, maintenance is easy, cost performance is high, and an image having high quality can be stably outputted.

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a sectional view showing a layer structure of an electrophotographic photoreceptor of the present invention.

FIG. 2 is a sectional view showing a layer structure of an electrophotographic photoreceptor of the present invention.

FIG. 3 is a sectional view showing a layer structure of an electrophotographic photoreceptor of the present invention.

FIG. 4 is a schematic view for explaining an electrophotographic process and an electrophotographic apparatus of the present invention.

FIG. 5 is a schematic view for explaining another example

of an electrophotographic process of the present invention.

FIG. 6 is a schematic view showing a process cartridge of an electrophotographic apparatus of the present invention

[Brief Description of Reference Symbols]

1, 6, 21: Photoreceptors

2: Diselectrification lamp

3: Electrification charger

5: Image exposing portion

6: Developing unit

: Pre-transfer charger

8: Resist roller

9: Transfer paper

10: Transfer charger

11: Separation charger

12: Separation pawl

13: Pre-cleaning charger

14: Fur brush

15: Cleaning blade

17: Electrification charger

18: Cleaning brush

19: Image exposing portion

20: Developing roller

22a, 22b: Driving roller

23: Charger

24: Image exposing source

25: Transfer charger

26: Pre-cleaning exposing light source

27: Cleaning brush

28: Diselectrification light source

31: Conductive support

33: Photosensitive layer

39: Protective layer

35: Charge generating layer

37: Charge transport layer

[FIG. 4]

1: Photoreceptor

2: Diselectrification lamp

3: Electrification charger

4: Cleaning blade

5: Fur brush

6: Pre-cleaning charger

7: Separation pawl

8: Separation charger

9: Transfer charger

10: Transfer paper

11: Resist roller

12: Pre-transfer charger

13: Developing unit

14: Image exposing part

[FIG. 5]

1: Electrification charger

2: Image exposing source

3: Photoreceptor

4: Driving roller

5: Pre-cleaning exposing

6: Driving roller

7: Diselectrification light source

8: Cleaning brush

9: Transfer charger

[FIG. 6]

1: Electrification charger

2: Image exposing portion

3: Cleaning brush

4: Photoreceptor

5: Developing roller

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F term (Reference)